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13. ABSTRACT *(Maximum 200 Words)*

Nanotubes have been targeted for potential applications ranging from the next generation of computers and flat-panel displays to structural and functional materials. In addition to their well-known stiffness (> 1 TPa) and strength (~30 GPa) properties, carbon nanotubes also possess exceptionally high electrical and thermal conductivities, with the axial thermal conductivity near that of crystalline diamond. The unique mechanical and physical properties of nanotubes offer tremendous opportunity for the development of multi-functional composites. Under this research program an integrated effort to processing, characterization, and analysis/modeling of nanotube-based composites was undertaken. Through this research work a fundamental understanding of the processing/structure/property relations in carbon nanotube-reinforced composites has evolved. Ultimately, the establishment of these basic relationships will enable the nanoscale design of nanotube-reinforced materials for Air Force and aerospace systems.

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MOTIVATION AND SCOPE

In composite materials, where distinct phases are combined together for reinforcement, the opportunity exists to design composites for specific properties at various levels of scale. For example, in traditional fibrous composites the engineer not only designs the geometric shape of the part but can prescribe the ply stacking sequence for lay-up, utilize different fibers to create hybrid composites, or bend and twist fibers together using textile techniques. At the microscopic scale, we are tailoring the local stiffness, strength, toughness and other properties through controlling the fiber orientation, type, and volume fraction. Recent advances in producing nanostructured materials with novel material properties have stimulated research to create macroscopic engineering materials by designing the structure at the nanoscale.

Since their observation in 1991 by Iijima [1], carbon nanotubes have been the focus of considerable research. At the nanometer scale, this unique form of carbon shows exceptional mechanical and physical properties with predicted elastic moduli of about 1 TPa (1000 GPa), strengths in the range of 30 GPa, and exceptional resilience, showing large nonlinear elastic deformation before fracture. Carbon nanotubes possess novel electronic properties, where they can be conducting or semi-conducting depending on the atomic structure, and have axial thermal conductivity that is predicted to be higher than diamond, the highest thermal conductivity of any known material. These properties, combined with their low density, fiber-like structure and high aspect ratio, have stimulated the development of nanotube-based composites. With potential applications ranging from molecular electronics and field-emission displays to nanocomposites, carbon nanotubes offer tremendous opportunity in the development of nanotechnologies.

As scientists and engineers seek to make practical materials and devices from nanostructures, understanding material behavior across length scales from the atomistic to macroscopic levels is required. Knowledge of how the nanoscale structure influences the nanotube properties as well as how nanotubes interact when embedded in a composite is needed to realize the potential for carbon nanotubes as reinforcement in composites. The change in reinforcement scale from microns of traditional fiber reinforcements to nanometers poses fundamentally new challenges in the processing, characterization and modeling of these materials.

In traditional fiber-reinforced composites, the properties of the constituent materials are first understood separately and then the materials are combined to examine the synergy [2]. Unlike traditional fibers, where the stiffness, statistical strength, and transport properties can be readily investigated with experimental techniques, obvious difficulties are encountered in testing nanotubes because of their size. In addition, the properties of carbon nanotubes, and nanostructured materials in general, are highly size/structure dependent and traditional continuum assumptions for nanotube and composite mechanical properties are not valid.

> The objective of this research program was to obtain a fundamental understanding of the processing/structure/property relations in carbon nanotube-reinforced composites through integrated research on processing and characterization of model nanocomposite systems as well as development of predictive models for the nanocomposite properties. Our integrated research approach is illustrated in Figure 1. Ultimately, the establishment of these basic relationships will enable the nanoscale design of nanotube-reinforced materials.
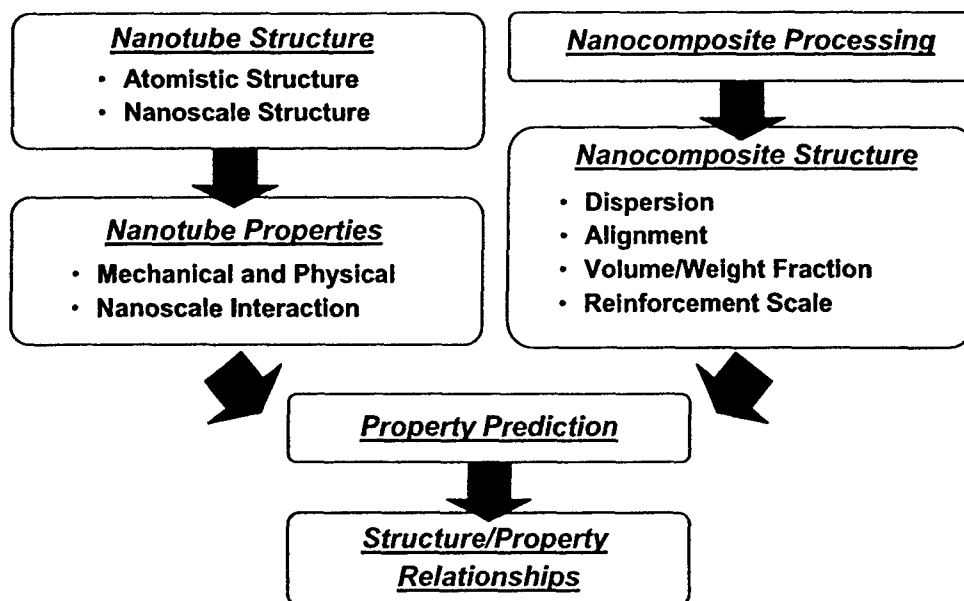
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│    Nanotube Structure        │        │   Nanocomposite Processing   │
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│  • Nanoscale Structure       │        │                              │
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│    Nanotube Properties       │        │   Nanocomposite Structure    │
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│  • Mechanical and Physical   │        │  • Alignment                 │
│  • Nanoscale Interaction     │        │  • Volume/Weight Fraction    │
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Figure 1: Research approach toward the development fundamental structure/property relationships for carbon nanotube-reinforced composites.

ALIGNED MODEL NANOCOMPOSITES

Toward the development of fundamental structure/property models for nanotube-reinforced composites, it is crucial to produce model nanocomposite systems with controlled structure. The key challenge is to obtain a nanotube composite where individual nanotubes are both dispersed homogeneously throughout the matrix phase and aligned in a primary direction. In this chapter, a processing technique is developed to produce model nanocomposites of multi-walled carbon nanotubes embedded in a polystyrene thermoplastic matrix. Continuous macroscopic ribbons of aligned nanocomposites were produced and the nanoscale structure of the composites characterized using electron microscopy and x-ray diffraction [3, 4].

For effective reinforcement, the nanotubes must be uniformly dispersed within the polymer matrix. Van der Waals interactions between the nanotubes often result in aggregates of nanotube ropes. In addition to slipping of tubes that are not adhered to the matrix, aggregates of nanotube bundles effectively reduce the aspect ratio of the reinforcement. Agglomeration is particularly significant in CVD-grown nanotubes, since substantial entanglement of the tubes occurs during nanotube synthesis. The difficulties in obtaining a homogenous dispersion of nanotubes are highlighted in recent scientific reviews by the authors [5, 6].

In this work, a novel technique is developed to produce highly aligned nanotube composite films. Solvent dispersion is utilized to obtain micron-scale dispersion of the nanotubes in the polymer matrix followed by melt compounding with a micro-scale twin-screw extruder to achieve nanoscale dispersion. The micro-scale compounding is able to provide the high shear mixing necessary to untangle the CVD-grown multi-walled nanotubes and disperse them uniformly in the thermoplastic polymer matrix. Highly aligned nanocomposite films can be produced by extruding the polymer melt through a rectangular die and controlled drawing of the film prior to solidification. Electron microscopy and x-ray diffraction results indicate that both the shear and extensional

flows result in significant process-induced alignment of the nanocomposite structure. The method of extruding and drawing the molten polymer creates a continuous ribbon of aligned nanocomposite that may then be laminated using traditional composites processing methods, such as autoclave molding or tape placement, to create macro-scale aligned nanocomposites.

The model nanocomposite system is composed of a polystyrene polymer matrix reinforced with CVD-grown multi-walled carbon nanotubes. The polystyrene used in this work is a commercially available thermoplastic with an average molecular weight of 280,000 (Scientific Polymer, Inc – Ontario, NY). The multi-walled carbon nanotubes used for the model nanotube-reinforced polymer composites were synthesized using conventional chemical vapor deposition (CVD) techniques. For the growth of carbon nanotubes, iron nanoparticles embedded in silica were used as the catalyst and the CVD process was carried out in a tube furnace [7]. The catalyst was heated under vacuum to a processing temperature of 700°C and nanotubes were grown for two hours under a flowing gas mixture of approximately 66% nitrogen (N_2), 27% ammonia (NH_3) and 7% acetylene (C_2H_2) at a pressure of 0.6 Torr [8]. The growth temperature and pressures were chosen so that the amounts of bamboo-like defects, where interior walls of the nanotube form internal caps along the length of the carbon nanotube, were minimized. After acid purification to remove residual impurities, the nanotubes were rinsed with distilled water and dried under vacuum for two hours at 120°C.

To achieve a homogeneous distribution of nanotubes in the polystyrene matrix, a processing method was developed that combines solvent-assisted dispersion of nanotubes in the polymer followed by shear mixing of the polymer melt using a micro-scale twin-screw extruder. Aligned nanocomposite films were formed by subsequently drawing the molten polymer prior to solidification and the extensional flow from drawing results in significant flow-induced alignment of nanotubes. Optimum processing parameters (mixing time, shear stress, draw ratio) to achieve a high degree of dispersion and alignment were determined experimentally by processing nanocomposite films using the micro-scale extruder and investigating the micro and nano-scale structure using transmission electron microscopy.

To examine the nanoscale structure of the aligned nanotube composites, samples were taken from along the length of the extruded ribbons for examination using TEM. Once samples were sectioned from the extruded nanocomposite, the films were embedded in an epoxy support and an ultramicrotome (Leica Ultracut UCT) with a diamond knife was used to cut slices for observation in the TEM. Figure 2 shows bright field TEM micrographs of the aligned nanocomposite films, and the arrows indicate the flow/drawing direction of the films. The gray lines visible in the TEM micrographs are artifacts from the cutting process caused by the diamond knife and indicate that the film was cut normal to the direction of nanotube orientation. The TEM micrographs show excellent dispersion of nanotubes within the polymer matrix. In addition, drawing the film from the melt resulted in substantial alignment of the nanotubes. Figure 2a shows large-scale dispersion and overall alignment of the carbon nanotubes and Figure 2b shows nanoscale tube alignment, particularly of the smaller diameter nanotubes not visible at lower magnifications.
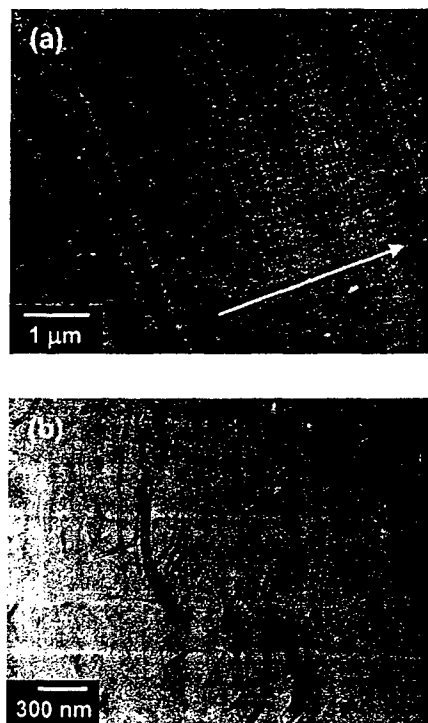
Figure 2: TEM micrographs of the aligned nanotube composite films showing large-scale dispersion as well as process-induced alignment of the reinforcement [3, 4].

Although electron microscopy is effective in directly investigating the nanoscale structure and orientation in nanotube-based composites, TEM is only able to survey very small volumes of the overall specimen. The thickness of the as-microtomed sections is approximately 200 nm (0.2 µm), and for adequate image resolution the largest area over which a TEM micrograph can be taken is on the order of a few square microns. In x-ray scattering, the incident beam interacts with a much larger volume of material and the scattering behavior can be utilized to gain insight into the micro and nanoscale structure of the composite.

At small angles, the length scale in nanotubes probed via x-ray scattering corresponds to the carbon nanotube diameters and can be used to examine the flow-induced orientation. Scattering measurements were performed on aligned and random nanocomposites as well as drawn polystyrene films. The specimens were rotated and translated between scans to ensure that the observed anisotropy in scattering was related to the bulk nanocomposite structure. Figure 3 shows schematics of the nanocomposite structure as observed via TEM and the related two-dimensional scattering patterns. The randomly oriented nanocomposite specimens (prepared by hot-pressing the dispersed nanocomposite into a film) show an isotropic, circular scattering pattern. The aligned nanocomposite specimens show anisotropic scattering. When the aligned nanocomposite specimens are oriented along the detector meridian or equator there is increased scattering in direction normal to the orientation, indicating that there is significant large-scale alignment of the carbon nanotubes.
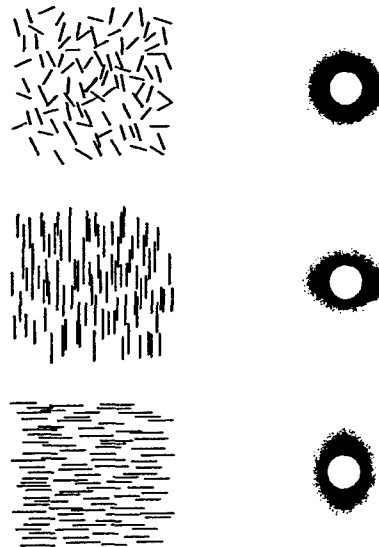
Figure 3: Schematics of the nanotube composite structure (left) and the corresponding two-dimensional SAXS patterns (right) [4].

NANOCOMPOSITE DEFORMATION AND FRACTURE BEHAVIOR

The aligned nanocomposite system forms a basis for our characterization and modeling research. Based on experimental characterization of the aligned model nanocomposite a micromechanical modeling methodology was developed to predict the elastic properties of the nanocomposite as functions of the constituent properties, reinforcement geometry and nanotube structure [9]. A fundamental understanding of their processing-structure-property relations has evolved [4, 9]. The nanoscale deformation and fracture mechanisms of the model nanocomposites are similar to those observed in traditional composites. Figure 4a shows a scanning electron microscope (SEM) image of a crack initiated in tensile loading of the aligned nanocomposite films, showing pullout of the carbon nanotubes as well as crack bridging. Figure 4b shows the fracture surface of the aligned nanocomposite. The fracture surface, which is tilted slightly to reveal the alignment and pullout length, shows aligned nanotubes protruding from the matrix. The overall pullout length is relatively constant and on the order of 100 nm. In Figure 4c, a TEM micrograph shows carbon nanotube pullout with matrix still adhered to the fractured tube, indicating good wetting and adhesion of the nanotubes with the matrix.
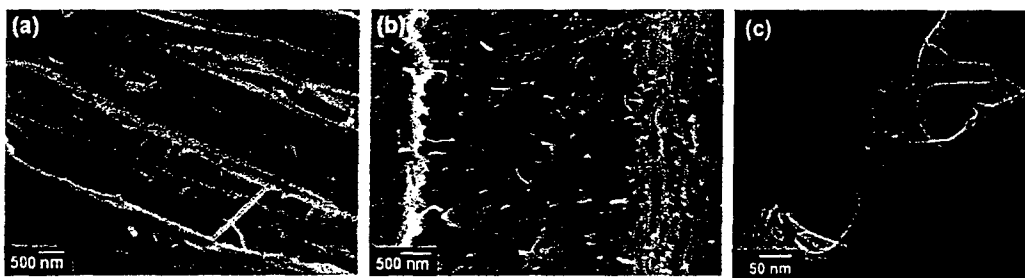

Figure 4: Micrographs of (a) a crack initiated during tensile fracture (b) the fracture surface of the aligned model nanocomposite and (c) nanotube pullout [3, 4].
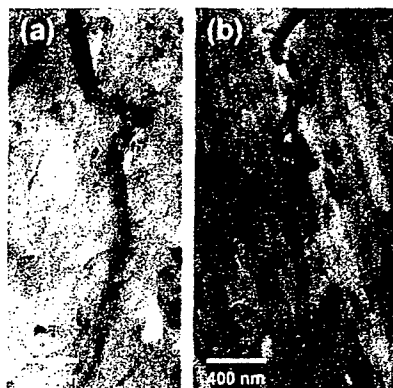
Figure 5: TEM micrographs of nanotube buckling in an aligned composite, (a) local nanotube buckling/kinking of a large diameter carbon nanotube and (b) segmental nanoscale buckling of a large diameter carbon nanotube at higher strain, indicating continued transfer of load to the nanotube after initial buckling [10].

While carbon nanotubes exhibit extraordinary resilience and flexibility at the nanoscale, it is not clear that these novel properties can translate to the macroscopic scales. To elucidate the nanoscale deformation behavior of carbon nanotubes in a polymer composite loaded in compression, a specimen geometry was developed to deform the aligned nanocomposites in axial compression. When loaded in compression, nanotubes show a transformation between Euler-type buckling for small nanotubes and local kinking for larger diameter nanotubes [10]. Critical nanoscale buckling was observed for the first time in this research work. Figure 5 shows TEM micrographs of large-diameter nanotubes deformed in compression, and, in some cases, large-diameter nanotubes buckle in multiple segments, indicating that the nanotube continues to carry load in compression after initial buckling.

STRUCTURE/PROPERTY MODELING OF NANOTUBE-BASED COMPOSITES

For modeling nanotube-based composites, it is important to consider the nano-scale structure of multi-walled carbon nanotubes as well as the load transferring from the matrix to the nanotube via shear stresses at the nanotube/matrix interface. A molecular structural mechanics approach developed for modeling carbon nanotubes [11] has been extended to model the effect of interfacial load transfer on the stress distribution in carbon nanotube/polymer composites using a multi-scale simulation [12]. For modeling of carbon nanotube-reinforced composites, the nanotube is modeled by the molecular structural mechanics method at the atomistic level and the matrix is modeled by the finite element method. The nanotube/matrix interface is assumed bonded either perfectly or by van der Waals interactions. The fundamental issues examined include the interfacial shear stress distribution, stress concentration in the matrix in the vicinity of nanotube ends, axial stress profile in the nanotube, and the effect of nanotube aspect ratio on load transfer.

To develop a fundamental understanding of the structure/size influence of carbon nanotubes on the elastic properties of nanotube-based composites, a micromechanical approach for modeling of short fiber composites was modified to account for the structure of the nanotube reinforcement to predict the elastic modulus of the nanocomposite as a function of the constituent properties, reinforcement geometry and nanotube structure. The micromechanics are then applied to the model system of multi-walled carbon nanotubes embedded in a polystyrene polymer matrix. The nanoscale structure and elastic properties of a model composite system of aligned multi-walled carbon nanotubes embedded in a polystyrene matrix were characterized and the experimental characterization results compared with numerical predictions that highlight

the structure/size influence of the nanotube reinforcement on the properties of the nanocomposite. The nanocomposite elastic properties are particularly sensitive to the nanotube diameter, since larger diameter nanotubes show a lower effective modulus and occupy a greater volume fraction in the composite relative to smaller diameter nanotubes.

We can express the nanocomposite elastic modulus in terms of the properties of the polymer matrix and the nanotube reinforcement [9]:

$$E_{11} = E_m \left[1 + 2\left(\frac{l}{d}\right) \frac{\left(\dfrac{E_{NT}}{E_m} - \dfrac{d}{4t}\right)}{\left(\dfrac{E_{NT}}{E_m} - \dfrac{l}{2t}\right)} V_{NT} \right] \left[1 - \frac{\left(\dfrac{E_{NT}}{E_m} - \dfrac{d}{4t}\right)}{\left(\dfrac{E_{NT}}{E_m} - \dfrac{l}{2t}\right)} V_{NT} \right]^{-1} \tag{1}$$

where, following standard notation used for traditional fibrous composites, E_{11} is the elastic modulus in the principal material direction, which is the direction of nanotube orientation, E_m is the matrix modulus, E_{NT} is the nanotube modulus, V_{NT} is the nanotube volume fraction, t is the nanotube wall thickness, l is the length and d is the nanotube diameter. Equation (1) is valid for $l > d > 4t$. Unlike traditional fibrous composites, where the aspect ratio completely describes the reinforcement in dimensionless terms, the nanotube diameter must be known since the reinforcement efficiency of the nanotube changes with diameter.

The distribution of nanotube diameters for a specific nanotube sample can be determined by measuring the outside diameter of a statistically large sample of nanotubes and then using the experimental data to determine the probability distribution of nanotubes $\xi(d)$. For the purpose of modeling the composite elastic properties, we are interested in the volume fraction of carbon nanotubes within the composite. From the diameter distribution we can then define the volume distribution of nanotubes per unit length $\psi(d)$:

$$\psi(d) = \frac{d^2 \xi(d)}{\displaystyle\int_0^\infty \left(d^2 \xi(d)\right) d(d)} \tag{2}$$

The above volume distribution will need to be considered when calculating the overall nanocomposite properties. Accurate modeling of the composite elastic modulus requires knowledge of the distribution of nanotube diameters and the volume fraction that tubes of a specific diameter occupy within the composite. If nanotubes are uniformly dispersed and aligned throughout the matrix phase, the contribution of each nanotube diameter can be considered to act in parallel. Therefore, the elastic modulus of the composite can be calculated as a summation of parallel composites over the range of nanotube diameters.

The concept of parallel composites is illustrated in Figure 6. Within the entire volume of the composite the volume can be divided into N individual composites containing a specific nanotube diameter. Each of the N individual composites will have a specific elastic modulus that depends on the local volume fraction of nanotubes at a given diameter. With the assumption of iso-strain, the elastic modulus of the composite can expressed as a summation of the moduli scaled by the partial volume of each nth composite:
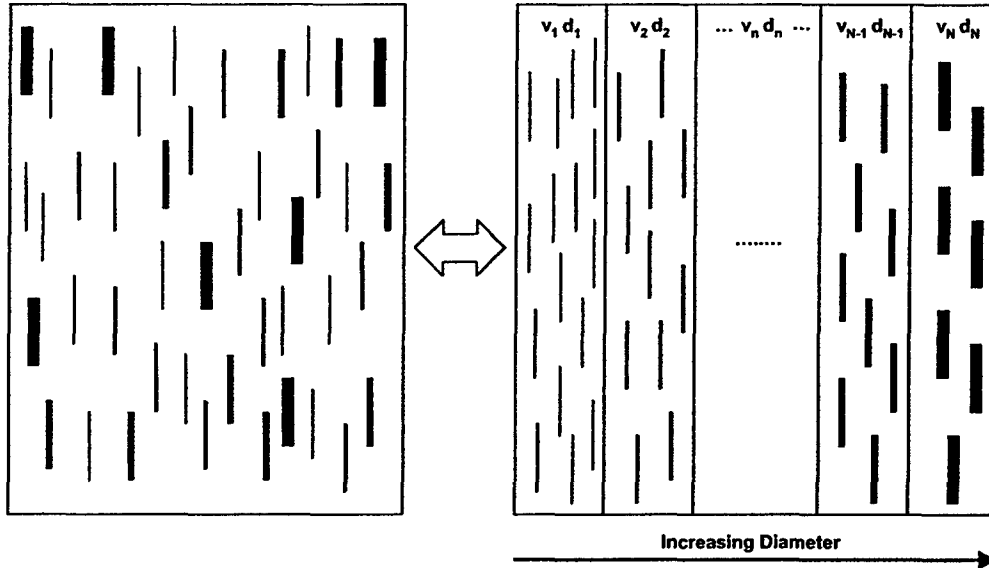
Increasing Diameter

Figure 6: The equivalence between a dispersed composite and N composites each with a specific nanotube diameter and partial volume acting in parallel [9].

$$E_c = \sum_{n=1}^{N} v_n E_n \big|_{d_n} \tag{3}$$

where $E_n \big|_{d_n}$ is the elastic modulus of the composite calculated from Equation (1) at the nanotube diameter included in the nth segment and v_n is the partial volume of the nth composite:

$$v_n = \frac{V_n}{V} \tag{4}$$

$$\sum_{n=1}^{\infty} v_n = 1 \tag{5}$$

where V_n is the volume of the nth composite and V is the overall composite volume.

　　To calculate the composite elastic modulus at a given nanotube diameter, E_n in Equation (3), the local volume fraction at a given nanotube diameter, $V_{NT}\big|_d$, can be calculated from the volume distribution of nanotubes (Equation 2).

$$V_{NT}\big|_{d_n} = \frac{\int_{d_n}^{d_n + \Delta d_n} \left(V_{NT} \psi(d) \right) d(d)}{v_n} \tag{6}$$

where V_{NT} is the total volume fraction of tubes in the composite and the limits of the integral are the range of diameters included in the nth composite.
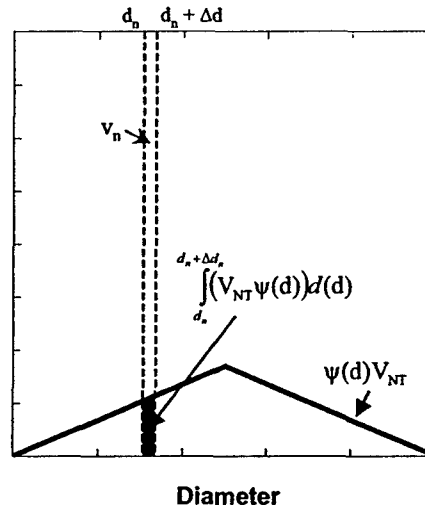
Figure 7: Graphical representation for the calculation of local nanotube volume fraction when given an arbitrary distribution in nanotube diameters [9].

The computation for the nanocomposite elastic modulus described in Equations (3-6) is illustrated schematically in Figure 7. Assume that the area within the axes of the graph represent a unit volume of the nanocomposite. The solid curve in Figure 7 is the product of some arbitrary nanotube volume distribution, $\psi(d)$, and nanotube volume fraction, V_{NT}, within the composite. Therefore, the shaded area beneath the curve represents the nanotube volume fraction. The nth composite is a narrow "slice" of the graph, represented by the dashed vertical lines, where there exists a narrow distribution of nanotube diameters Δd_n. The partial volume of the nth composite, v_n in Equation (4), is then the area between those dashed lines. Calculation of the local volume fraction of nanotubes in the nth composite is simply the area between the dashed lines underneath the solid curve divided by the total area between the dashed lines.

From the above modeling methodology to predict the elastic properties of the nanocomposite as functions of the constituent properties, reinforcement geometry and nanotube structure, a fundamental understanding of processing-structure-property in nanotube-based composites has been advanced [9]. For multi-walled carbon nanotubes, there will typically be a distribution of nanotube diameters in a given sample. Modeling the diameter distribution is particularly important because large diameter nanotubes show a lower effective stiffness and occupy a greater volume fraction in the composite relative to smaller diameter nanotubes. Figure 8 shows the experimentally measured diameter distribution and the probability density function for nanotube diameter, $\xi(d)$. From the diameter distribution we can then obtain the volume distribution of nanotubes per unit length $\psi(d)$. In the volume distribution, the relative area under the curve shifts to the larger diameters. To illustrate the importance of modeling the nanotube diameter distribution two models were used to fit the experimental data. For the Lorentz distributions, the calculated elastic modulus compares quite well with the results from the experimental characterization. The Gauss distribution, which ignores the contribution of the larger diameter nanotubes results in an overestimation of the composite elastic modulus, particularly at higher loading fractions.
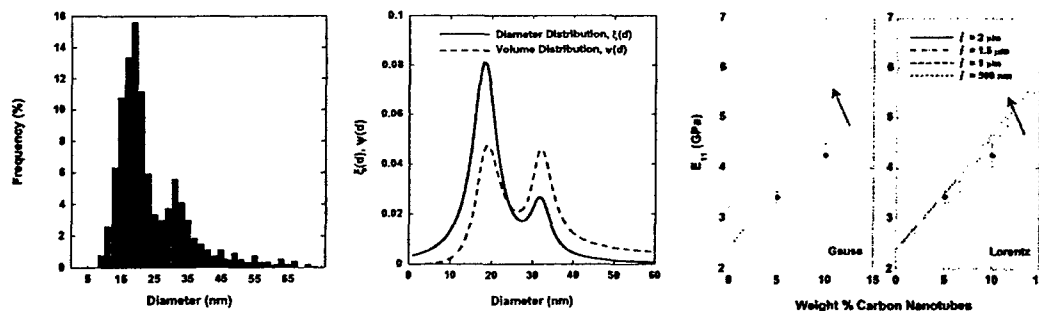
Figure 8: Influence of diameter distribution on the properties of nanocomposites [5].
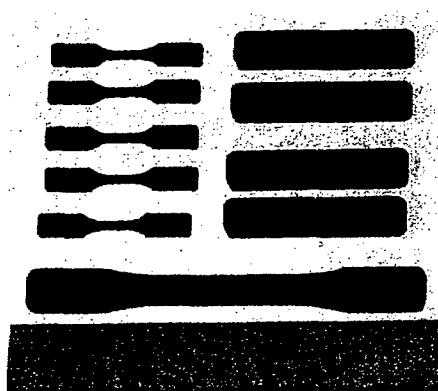

*Figure 9: Macroscopic nanotube composite test specimens
for property characterization.*

PROCESSING AND MECHANICAL/ELECTRICAL PROPERTIES OF NANOTUBE / EPOXY COMPOSITES

In order to evaluate such key engineering properties as strength, toughness and electrical/thermal conductivity it is crucial to fabricate more macroscopic nanocomposite test specimens. Acquisition of equipment for larger-scale production of nanocomposites from a recent AFOSR-supported DURIP grant has enabled us to address key scientific and technical issues associated with the scale-up processing of nanotube-reinforced composites. The volume of earlier batches of nanocomposites processed were around 4-6 cm^3. Recent batches have exceeded 150 cm^3. Different ASTM-standard-sized nanocomposite test specimens fabricated are shown in Figure 9.

Our recent research has also extended our capability to disperse nanotubes in thermosetting polymer matrices [13, 14]. Figure 10 shows TEM micrographs of randomly oriented dispersed nanotube composites in a thermoplastic (polystyrene) and thermoset (EPON 862) polymer matrix. After the initial dispersion of nanotubes in epoxy, the mixtures were processed using a laboratory-scale three-roll mill to achieve high shear stresses to break-apart the entangled nanotubes. The three-roll mill consists of three adjacent cylindrical rollers that each turns at a different velocity. The narrow gap, as low as 5 µm, combined with the mismatch in angular velocity results in intense shear mixing. Unlike other types of mills, which rely on compressive impact as well as shear, this approach results in nearly pure shear between the rolls. The nanotube/epoxy was passed-through the mill at progressively smaller gap settings until reaching the minimum and was processed at the minimum setting for several passes.
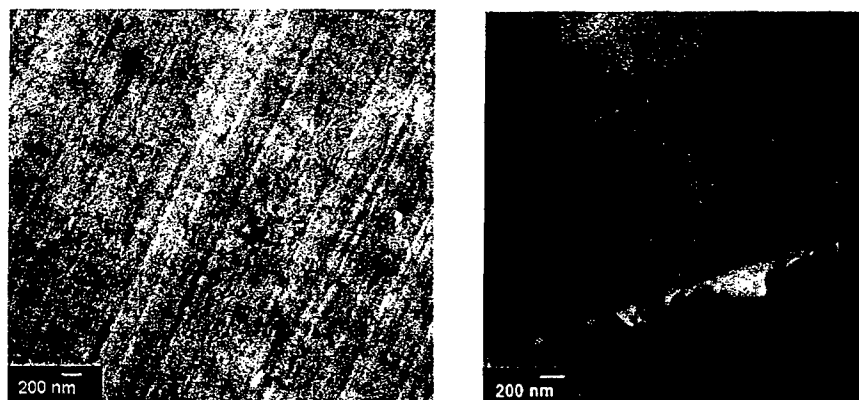
Figure 10: TEM micrographs showing nanotubes randomly dispersed in a polystyrene matrix (left) and EPON 862 epoxy matrix (right) [13].
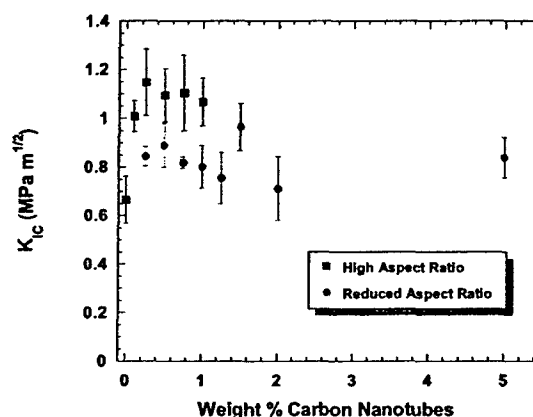

Figure 11: SENB fracture toughness results showing the influence nanotube content and morphology on the fracture toughness [13].

In order to evaluate the influence of multi-walled carbon nanotubes on the fracture toughness of epoxy nanocomposites we fabricated composites with nanotube contents ranging between 0.1 wt% and 5 wt% in an EPON 862 epoxy matrix. The nanotubes were first dispersed in the epoxy resin and the curing agent (Epi-Cure W) was added. The nanocomposites were then placed in a mold and cured for 6 hours at 130°C. Fracture toughness measurements were conducted using the single-edge-notch bending (SENB) method. Specimens were notched with a tapered diamond blade and a pre-crack was introduced by tapping with an ultra-sharp carbon steel razor blade. Figure 11 gives the fracture toughness results, showing significant increases in the fracture toughness with the addition of carbon nanotubes. This indicates that nanotubes provide a reinforcing effect in improving the fracture toughness through crack deflection or nanotube fracture and pullout. SEM micrographs of the composite fracture surfaces show a change in the micron-scale surface roughness and also the presence of nanotube pullout [13].

Carbon nanotubes have remarkably high electrical and thermal conductivities, offering potential for multi-functional reinforcement. The direct current electrical properties of the nanotube/epoxy composites were also investigated using a Keithley 6430 sub femtoamp remote sourcemeter. Electrical percolation transitions in the carbon nanotube/epoxy composites occur at concentrations below 0.1 wt%, (Figure 12) and nanotube/epoxy composites provide a level of electrical conductivity sufficient to permit electrostatic discharge.
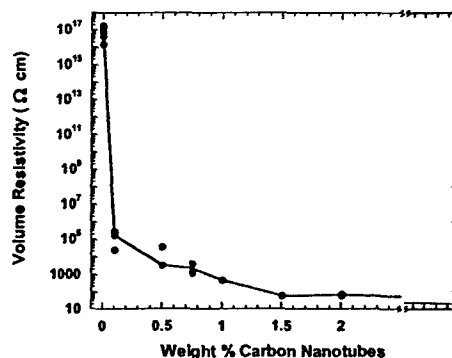

Figure 12: Electrical resistivity of carbon nanotube/epoxy composites [13].

FABRICATION AND CHARACTERIZATION OF NOVEL REACTION BONDED SILICON CARBIDE / CARBON NANOTUBE COMPOSITES

The extension of our processing technique to thermoset matrix materials has enabled the investigation of nanotube-reinforced ceramic matrix composites NT-CMCs. Nanotube-reinforced silicon carbide/carbon nanotube composites with nanotube volume contents ranging between 0.3 and 2.1% were fabricated by first creating a polymer composite containing dispersed nanotubes and silicon carbide particles. After carbonization of the matrix, molten silicon was infiltrated to produce reaction-bonded silicon carbide composites [14].

Figure 13 shows a high-resolution TEM micrograph (JEOL JEM 2010F) where a carbon nanotube is observed protruding from the matrix. The TEM results show conclusively that nanotubes both survived the melt-infiltration process where the graphitic layered structure of the carbon nanotube is maintained and the nanotubes are embedded in the ceramic matrix phase. In order to further understand the structure of the reaction-bonded nanocomposites and its influence on the electrical properties, a more detailed TEM investigation was undertaken. Figure 14 shows TEM micrographs (JEOL 2000FX) of the CNT 0.6% specimens that were prepared by thinning sections of the nanocomposites using mechanical polishing/dimpling followed by argon ion milling. Figures 14a to 14c show that carbon nanotubes are present in the as-processed composite and they are embedded in a continuous crystalline matrix phase. Nanotubes appear to be observed most frequently near the Si/SiC interfaces. Figure 14d shows a lower magnification TEM micrograph taken near the phase boundary, indicating that there may exist an "interphase" region between the Si and β-SiC where the nanotube concentration is highest.
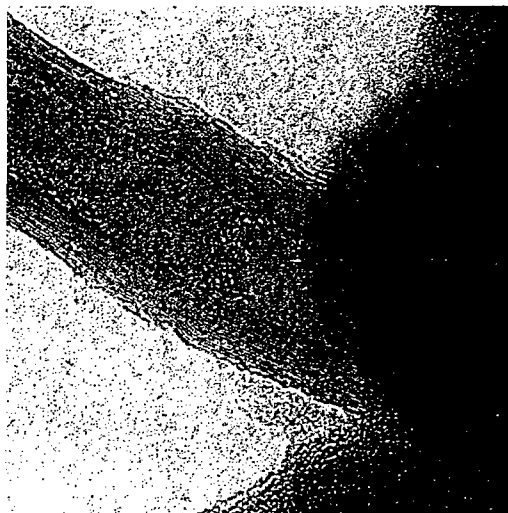
Figure 13: High-resolution TEM micrograph showing nanotubes in the reaction-bonded ceramic and the graphitic structure of the nanotube intact [14].
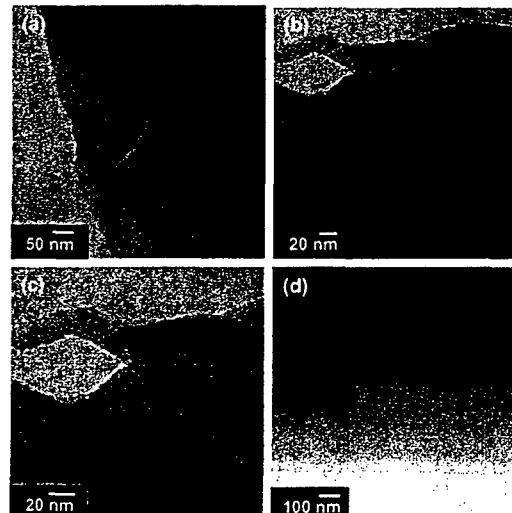
Figure 14: TEM micrographs showing nanotubes embedded in the continuous matrix and near the Si/SiC interfaces [14].
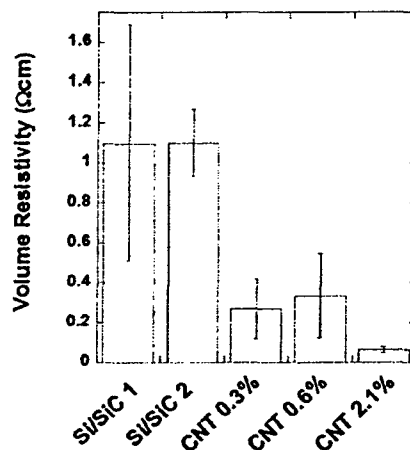

Figure 15: Influence of nanotube concentration on volume resistivity, showing a substantial decrease in resistivity with increased nanotube volume content [14].

There is a remarkable decrease in the electrical resistivity at these small nanotube loadings. With a volume content of just 0.3% carbon nanotubes there is a 75% decrease in electrical resistivity (Figure 15). At the highest nanotube volume content of 2.1%, there is a 96% decrease in electrical resistivity, which represents a 16-fold increase in electrical conductivity. While local variation in the micro-scale structure of the reaction-bonded ceramics results in some scatter of the resistivity data, the influence of adding carbon nanotubes on the electrical properties is unmistakable.

SUMMARY

The exceptional mechanical and physical properties demonstrated for carbon nanotubes, combined with their low density, make this new form of carbon an excellent candidate for composite reinforcement. Before these extraordinary properties observed at the nano-scale are realized in a macroscopic composite, considerable basic research is necessary. Full understanding of the thermo-mechanical behavior of nanotube-based composites, requires knowledge of the elastic and fracture properties of carbon nanotubes as well as interactions at the nanotube/matrix interface. Although this requirement is no different from that in conventional fiber composites the scale of the reinforcement phase diameter has changed from micrometer (e.g. glass and carbon fibers) to nano-meter. The change in reinforcement scale poses new challenges in the development of processing techniques for these composites as well as the development of characterization techniques and methodologies to measure the elastic and fracture behavior of carbon nanotubes and their composites. The nano-meter scale of the reinforcement presents additional challenges in mechanics research since we now must account for interactions at the atomic-scale.

Through this research, a novel technique that involves solvent-assisted dispersion followed by melt extrusion and drawing was developed to produce highly aligned nanotube composite films. The nanoscale structure of these continuous macroscopic ribbons of nanocomposites was investigated using electron microscopy and x-ray diffraction. The combination of both high shear mixing imparted by the extrusion process and extensional flow results in a high degree of nanotube alignment in the polymer matrix. Alignment of the nanotubes by drawing from the polymer melt resulted in significant improvements in elastic modulus as compared with the randomly oriented nanotube composites.

The fracture of the model nanocomposites exhibits nanoscale fracture mechanisms that are similar to those observed in traditional composites. While carbon nanotubes exhibit extraordinary resilience and flexibility at the nanoscale, it is not clear that these novel properties can translate to the macroscopic scale. Particularly in compression, carbon nanotubes show large, nonlinear deformation before fracture, but in engineering applications such large deformation would not be realized until the structure had deformed past its design limit. In this work, we showed the nano-scale buckling behavior of carbon nanotubes utilized as reinforcement in an engineering material exhibit a transformation between Euler-type buckling for small nanotubes and local kinking for larger diameter nanotubes.

In the literature on nanotube-based composites, there is large variation in the reported elastic properties, but little information is supplied concerning the nanocomposite structure. Reported improvements in elastic modulus are lower than expected if the nanotube is assumed to act as a solid fiber with an elastic modulus of 1 TPa. Discrepancies are often explained by assuming that there is insufficient load transfer at the nanotube/matrix interface. While a strong interface between the reinforcement and matrix is important in terms of load transfer efficiency, improvements in interface properties have a far greater influence on the composite ultimate strength and fracture behavior than the elastic moduli at low strain. Results from our micromechanics modeling show the diameter and nanoscale structure of the carbon nanotube plays a significant role in transfer of load within the composite, and variations in reported elastic properties are likely a consequence of (1) differences in the structure and size of the nanotubes used as reinforcement and (2) variations and lack of control of the nanocomposite structure.

Our recent research on nanotube-reinforced epoxy composites has demonstrated enhanced fracture toughness at relatively low carbon nanotube loading contents. Furthermore, the electrical percolation threshold in these composites occurs at extremely low carbon nanotube concentrations. We have also recently fabricated novel silicon carbide/carbon nanotube ceramic composites using a thermosetting resin as a precursor. Substantial decreases in electrical resistivity at low nanotube concentrations were also observed in the nanotube-reinforced ceramics. Microscopy results indicate that the graphitic structure of the carbon nanotubes remain intact after the high temperature processing.

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